Lecture 25: Molecular Orbital Theory of Diatomic Molecules. II

In 5.111/5.112 we use orbital energies and shielding arguments to rationalize the Periodic Table. All properties, all atoms: IP, Electronegativity, size (via IP and modified Rydberg formula).

My personal vision has been to extend the periodicity of electronic properties from atoms to molecules. This lecture and a significant part of Exam III is constructed around that vision.

This lecture is intended to enable you to intuit the properties of $\text{H}_2$, $\text{AH}$, $\text{A}_2$, and $\text{AB}$ diatomic molecules. Larger molecules would follow.

Toy Models — naive but SMART approximations

Semi–Empirical calculations — to calibrate the Toy Model based on atomic energy levels, atomic sizes, and qualitative lessons learned from the $\text{H}_2^+$ LCAO-MO model.

Orbitals: Pictures, Names, Bonding/Anti-bonding Properties

bonding is due to constructive interference that arises from overlap, $S$, in the region between the 2 nuclei
Bond strength is roughly proportional to overlap

\[ S_{n\ell\lambda}(R) = \int n\ell\lambda_A(\vec{r}_A; R)n\ell\lambda_B(\vec{r}_B; R)d\tau. \]

The molecular orbital is bonding if 2 atomic orbitals in the overlap region have same phase, anti-bonding if they have opposite phase.

**σ** \(_g\) (\(ns\))

\[ ns_A + ns_B \]

anti-bonding

**σ** \(_u\) (\(ns\))

\[ ns_A - ns_B \]

Body frame \(g,u\) inversion symmetry (\(g = gerade\) or even, \(u = ungerade\) or odd)

* is extra notation (optional) for anti-bonding

**σ** \(_g\) (\(np\))

\[ np_{z,A} - np_{z,B} \]

**σ** \(_u\) (\(np\))

\[ np_{z,A} + np_{z,B} \]

**π** \(_u\) (\(np\))

\[ np_{y,A} + np_{y,B} \]

**π** \(_g\) (\(np\))

\[ np_{x,A} - np_{x,B} \]
What did we learn from $\text{H}_2^+$?

$\text{IP}_{\text{H}}$

$\sigma_g(1s)$ less bonding than $\sigma_u^*(1s)$ is anti-bonding

$\text{IP (H}_2^+) \ X^2\Sigma_g^+ \sim \text{IP (H)}$ plus bonding ($\text{D}_e^c$) stabilization due to one $e^-$ in $\sigma_g(1s)$

Electronic Ground state in $\sigma_g(1s) \ X^2\Sigma_g^+$ is bound!

Excited state $A^2 \Sigma_u^+$ is repulsive

$$R_e(\text{H}_2^+) < 2 \langle r \rangle_{\text{H} \ 1s}$$

Minimal Basis Set Variational Calculation

(what is the Variational Theorem?)

2 AO's → 2 MO's

minimize $E_{avg}$

determine ground state $E(R)$ and $R_e$ (equilibrium internuclear distance)

more variational functions would give more accurate values. Requires computer.

Trust our model for qualitative insights
Extrapolate from $\text{H}_2^+$ to $\text{H}_2$. What happens to molecular properties if we add another $e^-$

- get $R_e$ decrease by $\sim 30\%$
- get $\omega_e$ increase by $\sim 90\%$ (vibrational frequency)
- get $D_e^e$ (dissociation energy) increase by $\sim 70\%$

concept of “bond”. Go from $1/2$ bond to full bond.

In chemistry we think of a bond as involving $2e^-$. Why not 1 or 3? You can put $2e^-$ into one orbital $(\alpha\beta - \beta\alpha)$ but not $3e^-$. 

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**More on $\text{H}_2^+$**

The $1s_A, 1s_B$ basis set gave (McQuarrie)

$$
S(R) = e^{-R} \left( 1 + R + \frac{1}{3} R^2 \right)
$$

$$
H_{12}(R) = e^{-R} \left( \frac{1}{R} - \frac{1}{2} - \frac{1}{6} R - \frac{1}{6} R^2 \right)
$$

at large $R$, $S$ is driving force for bonding

$$
\varepsilon(R) = -\frac{1}{2} + e^{-2R} \left( 1 + \frac{1}{R} \right)
$$

$E_{\text{H}(1s)}$ bare H$^+$ penetrates inside H atom. Sees repulsion by progressively less-shielded nucleus as $R$-decreases.

Everything is atom-like at large-$R$

Bonding begins as $R$ decreases, initially $\propto S$

Bonding turns around and is cancelled by overlap repulsion at short $R$ [at what $R$ would you expect this to begin to be important?]

$$
R < 2 \langle r \rangle_{n\ell} \quad (z \text{ direction})
$$
Short step from $H_2^+$ to $H_2$ to $A_2$

How many $e^-$?

Feed $e^-$ into lowest orbitals following “exclusion principle”

Configuration: list of occupied orbitals

Excited configurations too $\rightarrow$ excited states

Configurations can give rise to several electronic states, as for $\text{He}(1s \, 2s) : ^1S + ^3S$

$$\text{for } H_2 \quad X^1\Sigma_g^+ \quad \sigma_g(1s)^2 \quad \text{bound}$$

$$a^3\Sigma_u^+ \quad \sigma_g(1s)\sigma_u^*(1s) \quad \text{repulsive}$$

There could also be $\sigma_g, \sigma_u, \pi_g, \pi_u$ orbitals arising from $2s, 2p$

These $n = 2$ orbitals are much less bonding/anti-bonding: WHY?

orbital size, much smaller $S$ at $R_e$ of $X^1\Sigma_g^+$ ground electronic state

**$H_2 \rightarrow AH$ (NH as example)**
AO Energies (from Atomic Spectra) [Semi-Empirical]

<table>
<thead>
<tr>
<th>Atom</th>
<th>1s</th>
<th>2s, 2p</th>
<th>1s</th>
<th>2s</th>
<th>(2p)</th>
<th>( N(2p) )</th>
<th>( N(2s) )</th>
<th>( N(1s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IE</td>
<td>13.6 eV</td>
<td>3.4 eV</td>
<td>&gt; 100 eV</td>
<td>( \sim 18 ) eV</td>
<td>( \sim 12 ) eV</td>
<td>( \sim 18 ) eV</td>
<td>( \sim 100 ) eV</td>
<td>( \sim 13.6 ) eV</td>
</tr>
</tbody>
</table>

Total number of \( e^- = 8 \). Look at order of IE to guide the order in which orbitals are filled. 2\( e^- \) in \( N(1s) \), 2\( e^- \) in \( N(2s) \), 2\( e^- \) in \( H-N 1s\sigma - 2p\sigma \) strong covalent bond, 2\( e^- \) in Non-BONDING \( N(2p\pi) \)

We have

\[
\sigma^2 \sigma^2 \pi^2 \quad \sigma^2 \quad \pi^2 : \Sigma^- , \Delta , \Sigma^+ \text{ electronic states}
\]

atom-localized → bonding → non-bonding

Predict \( IP(NH) = IP[N 2p] + D^e_\epsilon \)

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**LCAO-MO for \( A_2 \)**

**Li\( _2 \ldots \) F\( _2 \)**

Always in textbooks

To begin — look up (from atomic spectra)

Atom \( A 2p, 2s \) AO energies relative to \( A^+ \)

Now to build a PRIMITIVE LCAO-MO diagram.

This is intentionally naive because it requires addition of extra effects, based on some empirical observations on a few systems generalized to many systems.
Rydberg States
\( n > 2 \)
(too high-lying to contribute to bonding)

Facts: 2s smaller than 2p because of higher Ionization Energy, hence smaller size. Overlap starts at smaller \( R \). \( \sigma_g(2p) \) more bound than \( \pi_u(2p) \) overlap because p orbital is extended along \( z \).
\( \sigma_g(2s) \) and \( \sigma_g(2p) \) have same \( \sigma_g \) symmetry so they can interact. Also true for 
\[ \sigma_u^*(2s) \text{ and } \sigma_u^*(2p). \]

Also \( \pi_u, \pi_g^* \) have no \( \pi \) orbital below — no upward shift due to repulsion from below.

Why does \( \sigma(2s) \sim \sigma(2p) \) interaction change as we go across period Li→F?

Atom ion-core shielding effects cause an increase in \( s, p \) energy gap.
(Down-shift of $\sigma_g(2s)$ relative to $\sigma_g(2p)$ as 2s sees larger increase in $Z_{\text{eff}}$ as Li→F)

$$\Delta H = \begin{pmatrix}
\varepsilon_p & V_{ps} \\
V_{ps} & \varepsilon_s
\end{pmatrix}$$

$$\varepsilon = \frac{\varepsilon_p + \varepsilon_s}{2} \pm \left[ \Delta \varepsilon^2 + V_{ps}^2 \right]^{1/2}$$

$$\Delta \varepsilon = \frac{\varepsilon_p - \varepsilon_s}{2}$$

$$\varepsilon = \frac{\varepsilon_p + (\varepsilon_s - \Delta)}{2} \pm \left[ (\Delta \varepsilon + \Delta)^2 + V_{ps}^2 \right]^{1/2}$$

Repulsion shift from nominal pattern decreases Li→F

toward nominal $\sigma_g < \pi_u$, O,F
starts out $\pi_u < \sigma_g$, Li . . . N
inverted

Crude interpretive use of non-degenerate perturbation theory:

for A-A $\varepsilon_{n\ell\lambda}^{A} = \varepsilon_{n\ell\lambda}^{A}$

$$V_{n\ell\lambda}^{AA} = \frac{1}{2}(n\ell\lambda^* - n\ell\lambda).$$

R-dependent energy difference between anti-bonding and bonding orbital.

For A-B $\varepsilon_{n\ell\lambda}^{A} \neq \varepsilon_{n\ell\lambda}^{B}$.

Use this $V_{n\ell\lambda}^{AA}$ to guess value of $V_{n\ell\lambda}^{AB}$

$$V_{n\ell\lambda}^{AB} = \int \psi_{n\ell\lambda}^{\circ} \hat{H}^{(1)} \psi_{n\ell\lambda}^{\circ} d\tau$$

Alternatively, could estimate $V_{n\ell\lambda}^{AB}$ from

$$\left[ \left( V_{n\ell\lambda}^{AA} \right) \left( V_{n\ell\lambda}^{BB} \right) \right]^{1/2}$$
So from $\varepsilon_{n\ell\lambda^*} - \varepsilon_{n\ell\lambda} = 2V_{n\ell\lambda}^{AB}$ now we can use this semi-empirical value of $V_{n\ell\lambda}^{AB}$ to predict $V_{n\ell\lambda'}^{AB}$ for some molecule guided by orbital size (orbital ionization energy) or $S(R)$ overlap or for neighboring $AB$ molecules where

$$
\begin{pmatrix}
\varepsilon_{n\ell\lambda_A}^{(0)} \\
\varepsilon_{n\ell\lambda_B}^{(0)} \\
V
\end{pmatrix}
\begin{pmatrix}
\varepsilon_{n\ell\lambda_A} \\
V
\varepsilon_{n\ell\lambda_B}^{(0)}
\end{pmatrix}
= 2V_{n\ell\lambda}^{AB}
$$

Orbital Energy Order

- $\varepsilon_{\sigma_g(2p)} > \varepsilon_{\pi_u(2p)}$ for $\text{Li, } \ldots, \text{C}$
- $\varepsilon_{\pi_u(2p)} > \varepsilon_{\sigma_g(2p)}$ for $\text{N, O, F}$

8 valence $e^-$

- $\text{C}_2 \quad X^1\Sigma_g^+ \quad \sigma_g^2 \sigma_u^2 \pi_u^4 \quad \pi_u(2p) < \sigma_g(2p)$
- $a^3\Pi_u \quad \sigma_g^2 \sigma_u^2 \pi_u \sigma_g$

10 valence $e^-$

- $\text{N}_2 \quad X^1\Sigma_g^+ \quad \sigma_g^2 \sigma_u^2 \sigma_g^2 \pi_u^4$
- $A^3\Sigma_+^+ \quad \sigma_g^2 \sigma_u^2 \sigma_g^2 \pi_u^3 \pi^*_g$
- $B^3\Pi_g \quad \sigma_g^2 \sigma_u^2 \sigma_g^2 \pi_u^4 \pi^*_g$

So we can explain, anticipate, and exploit predicted "anomalies".
Unequal sharing of orbitals from $A$ vs. $B$.

Use non-degenerate perturbation theory to estimate:

- fractional $A, B$ character in orbital
• polar bonding

• sign of polarity depends on number of $e^-$

• vs. equal sharing for $A_2$ molecules

• how does a molecule bind to a metal surface? positive end down, negative end down, lying down?